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5f State Interaction with Inner Coordination Sphere Ligands: Einsteinium 3+ Ion Fluorescence in Aqueous and Organic Phases

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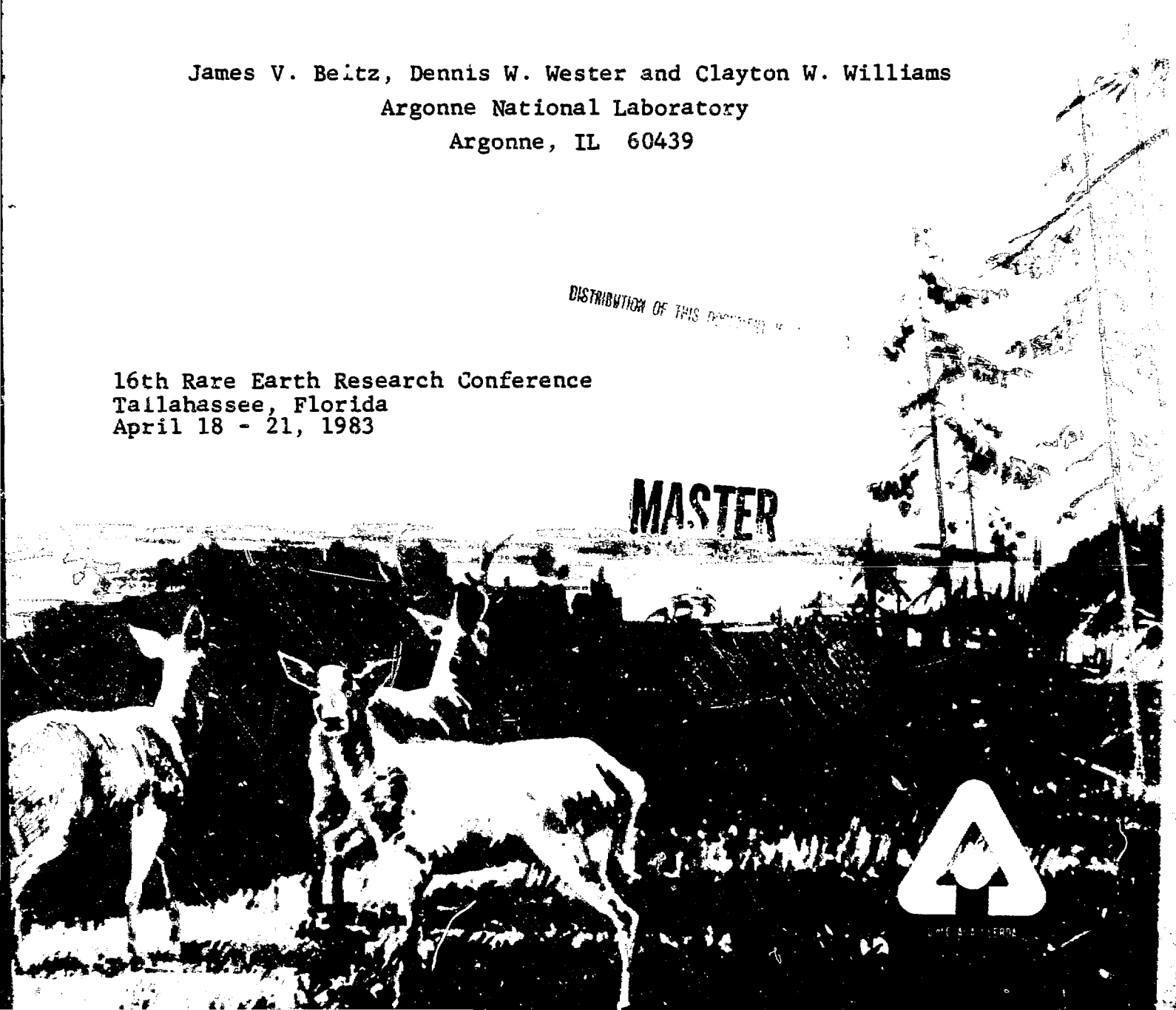

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A HERD OF SMALL WHITE DEER (A RARE MUTATION OF THE FALLOW DEER, DAMA DAMA) ROAM THE ARGONNE GROUNDS. THE DRAWING ON THE COVER SHOWS THREE OF THESE UNUSUAL ANIMALS.

5f State Interaction with Inner Coordination Sphere Ligands: Einsteinium 3+ Ion Fluorescence in Aqueous and Organic Phases

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ABSTRACT

The interaction between 5f electron states of einsteinium 3+ ion and coordinated ligands in solution has been probed using laser-induced fluorescence. Aquo einsteinium 3+ ion was observed to fluoresce from its first excited J = 5 state in a broad-band peaking at 9260 wavenumbers. The observed fluorescence lifetimes were 1.05 microseconds and 2.78 microseconds in H_2O and D_2O (99+ % D atom), respectively. The non-radiative decay rates derived from the lifetime data are compared with previously reported data for Cm, Sm, Eu, Tb, and Dy aquo 3+ ions. The 5f actinide states exhibit substantially greater non-radiative decay rates than do lanthanide 4f states of similar energy gap. This provides evidence that actinide 5f electrons interact more strongly with their inner coordination sphere than do lanthanide ion 4f electrons. The fluorescence lifetime of einsteinium 3+ ion complexed with 1 formal di(2-ethylhexyl)orthophosphoric acid in n-heptane was 2.34 microseconds.

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The availability of microgram quantities of ^{253}Es made possible the first optical absorption studies of aquo einsteinium 3+ ion over a decade ago [1]. Subsequent studies [2,3] established the general ordering expected for the 5f states and indicated that the largest energy gap between Es^{3+} 5f states would occur between the ground state manifold and the first excited 5f state. Optical absorption studies of aquo Es^{3+} failed, however, to observe the first excited 5f state. Fluorescence from this state was observed from Es^{3+} doped into crystals of a CsGd-diketone chelate by Nugent and co-workers who concluded that the corresponding transition would occur at 9600 cm^{-1} for aquo Es^{3+} [4]. The only larger energy gap transition among An^{3+} 5f states occurs in Cm^{3+} [5].

The free-ion energy level structure calculation and Judd-Ofelt intensity analysis of the available Es^{3+} solution spectra by Carnall and co-workers [3] provided a rationale for the failure of optical absorption studies to observe the ground state to first excited 5f state transition as the transition intensity was predicted to be extremely weak. Studies of Es^{3+} doped into $LnCl_3$ crystals carried out by Hessler and co-workers [6] have accurately measured the 5f state energy level structure of Es^{3+} including the position of the first $J = 5$ state and recent refinements [7] of Judd-Ofelt intensity parameters for heavy An^{3+} ions have extended radiative lifetime and branching ratio calculations for An^{3+} 5f states across the transuranic series to Es.

The fluorescence properties of aquo actinide 5f states are of considerable fundamental interest as 5f electrons are expected to undergo larger interaction with surrounding ligands than are lanthanide ion 4f electrons due to the larger radial extent of 5f electron wavefunctions. The only previous study [8] of 5f state fluorescence from an aquo transuranic 3+ ion involved a transition in Cm^{3+}. The aquo Cm^{3+} non-radiative decay rate found was substantially larger than those reported for similar energy gap aquo lanthanide ion 4f transitions. Our observation of fluorescence from aquo Es^{3+} is therefore an unusual opportunity to explore An^{3+} 5f state non-radiative decay rates in the large energy gap regime and extends the comparison of Ln^{3+} and An^{3+} non-radiative decay rates in solution.

EXPERIMENTAL METHODS

^{253}Es was obtained from Oak Ridge National Laboratory. The "as received" Es was used in a few experiments, but in most experiments the Es had been recently separated from its principal decay daughter, ^{249}Bk. Due to the 20.47 day halflife of ^{253}Es, a liquid extraction technique was used to remove the Bk. This was achieved by selectively oxidizing the Bk^{3+} to Bk^{4+} using bromate in nitric acid. The Bk^{4+} was then extracted into an organic phase. No dependence of the observed Es^{3+} fluorescence lifetime on Bk^{3+} concentration was found (maximum Bk/Es ratio about 1). The intense radioactivity of the more concentrated solutions of Es^{3+} lead to

formation of gas bubbles which limited the accuracy with which Es^{3+} concentrations were known. The H_2O and D_2O used were triple distilled [9]. The isotopic purity of the DCl solutions with respect to deuterium was measured to be better than 99 atom %. A sample of Es^{3+} complexed with di(2-ethylhexyl)orthophosphoric (HDEHP) was prepared by extracting Es^{3+} from aqeuous solution using 1 formal HDEHP in n-heptane. The sample solutions were contained in UV-grade, quartz cells (typically 3 x 9 mm rectangular cross-section).

Two different dye laser systems were used during the course of this work: a nitrogen laser pumped dye laser producing typically 0.2 mJ/pulse and a tripled Nd:YAG pumped dye laser producing up to 15 mJ/pulse. Both a 77 K InAs infrared detector and a cooled S-1 photomultiplier were used as fluorescence detectors with f/1 light collection optics. The output from the detector in use was amplified and a digital transient recorder-signal averager system was used to measure the fluorescence intensity decay curve. A linear least squares analysis was used to obtain the lifetime of the fluorescing state. Fluorescence lifetimes were measured using the S-1 photomultiplier (detection system 1/e response time: 50 ns) with long pass optical filters to block scattered laser light. The InAs detector, a 25 cm f.l. monochromator (590 g/mm grating blazed at 1000 nm) and long pass filters were used to measure the fluorescence emission spectrum of aquo Es^{3+}. It was necessary to use the InAs detector inspite of its substantially lower detectivity

since the S-1 photomultiplier's response fell off very steeply at long wavelengths.

RESULTS

FLUORESCENCE EMISSION SPECTRUM - A low resolution fluorescence excitation spectrum was first recorded which peaked at 495 nm in good agreement with the reported spectrum of Es^{3+} [3]. The nitrogen laser pumped dye laser was then set to 495 nm and the fluorescence emission spectrum was measured. The spectral region effectively scanned was from 860 nm to 1550 nm (10% transmission limits). The sample contained about 1 x 10^{-3} mol/dm^3 Es^{3+} in 0.6 mol/dm^3 DCl solution. The spectral response function [10] of the detection system was obtained using a tungsten lamp whose filament temperature was measured with an optical pyrometer. The corrected fluorescence emission spectrum is shown in Figure 1. The spectral bandpass indicated is the experimentally measured full width half maximum response bandpass of 240 cm^{-1} (1 cm^{-1} = 0.011963 kJ/mole). The fluorescence intensity uncertainity shown is the maximum deviation of the spectral response corrected data from the smooth line curve shown.

FLUORESCENCE LIFETIME MEASUREMENTS - Measurements of fluorescence lifetimes were carried out for Es^{3+} in both HCl and DCl solutions and for Es^{3+} complexed with HDEHP in n-heptane. The results obtained are shown in Table I. It is evident that the

highest concentration of Es^{3+} resulted in an observable shortening of the fluorescence lifetime. In all cases the data were well-fit using a single exponential decay model. At the lowest Es^{3+} concentration some interference arose from fluorescence from optical filters which were used to block scattered laser light. The filter fluorescence was found to exhibit complex (i.e. multiple exponential) fluorescence intensity decays.

DISCUSSION

The energy level diagram shown in Figure 2 is based on the calculations of Carnall and co-workers [3] and has largely been confirmed by the experimental observations of Hessler and co-workers [6]. Based on this energy level diagram, the observed Es^{3+} fluorescence emission spectrum shown in Figure 1 is readily assigned as arising from the first $J = 5$ state at 9584 cm^{-1}. Non-radiaitive decay most likely occurs as a cascade down the 5f state manifold. Other energetically possible transitions such as from the $J = 5$ state at 18900 cm^{-1} to the $J = 5$ state at 9584 cm^{-1} are ruled out due to the small energy gaps to next lower states, the absence of multiple fluorescence emission bands and the observed single exponential fluorescence intensity decay. The width of the corrected fluorescence spectrum, 1120 cm^{-1}, is quite large in comparison with the 455 cm^{-1} ground state crystal field splitting observed in a $LnCl_3$ host [11], even when both the spectral bandpass (240 cm^{-1}) and the average thermal energy of the aqueous

solution (205 cm^{-1}) are subtracted. The corrected fluorescence emission spectrum of aquo Es^{3+} shown in Figure 1 peaks at 9260 cm^{-1} in good agreement with the J = 8 to J = 5 separation of 9584 cm^{-1} found for Es^{3+} in $LnCl_3$ host (allowing for the 455 cm^{-1} splitting of the J = 8 ground state).

A significant fraction of the Es^{3+} was probably present as an outer sphere complex based on the stability constants reported by Harmon et al [12]. From their work, we would expect that as much as 50% of the Es^{3+} in our hydrochloric acid solutions may have been present as an outer sphere complex with Cl^- (i.e. as $EsCl^{2+}$ where one or more water molecules separate the Es^{3+} cation from the Cl^- anion). Since 5f electrons are formally non-bonding electrons with little radial extent beyond the first coordination sphere, it is likely that such outer sphere complexation has little effect on the observed fluorescence emission spectrum or lifetimes. Indeed the fluorescence spectra and lifetimes of Cm^{3+} in perchloric and hydrochloric acid solutions [8] are the same to within experimental error for acid concentrations similar to those used in the present work.

The radiative lifetime of the aquo Es^{3+} emitting J = 5 state has been calculated to be 2.4 ms based on a Judd-Ofelt intensity parameter analysis of heavy 3+ actinides [7]. Based on this value and the data in Table I, the fluorescence quantum yield to be expected from the J = 5 state at 9584 cm^{-1} is about 0.0001, if the

state is directly populated. In our experiments, where we populated a much higher lying 5f state and relied on non-radiative decay to populate the fluorescing state, the actual quantum yield may have been much less. Since there are no branching ratio problems, the following simple relationship exists between the non-radiative decay rate constant, k_{nr}, and the observed fluorescence lifetime, t_{obs}:

$$k_{nr} = 1/ t_{obs} \quad (1)$$

From the lifetimes shown in Table I, it is evident that in sufficiently dilute $^{253}Es^{3+}$ solutions a sensibly constant lifetime is found. At higher Es concentrations radiolysis products evidently acts as fluorescence quenchers. Using Eqn 1 we find that k_{nr} (in sec^{-1}) for aquo Es^{3+} in DCl solutions is 3.6×10^5 and is 9.5×10^5 for Es^{3+} in HCl solution. Non-radiative decay of Es^{3+} complexed with HDEHP in n-heptane occurs with a value of k_{nr}, 4.3×10^5 sec^{-1}, which is intermediate between that found for the DCl and HCl solutions. This suggests the possible participation of relatively high frequency ligand vibrational modes, such as C-H stretches, in the non-radiative decay of Es^{3+} complexed with HDEHP.

Figure 3 compares the present Es^{3+} data to previously reported non-radiative decay rates for Cm^{3+} [8] and for aquo Ln^{3+} ion transitions with similar energy gaps. The lanthanide ion data are from Stein and Wurzberg [13]. It is evident that both Es and Cm show substantially larger non-radiative decay rates than do

lanthanides of similar energy gap, suggesting a greater degree of interaction between the actinide and its inner coordination sphere. The solid and dashed lines in Figure 3 result from linear least square fits of the actinide and lanthanide data, respectively, to the following equation:

$$k_{nr} = C \exp(aE) \qquad (2)$$

where C and a are constants characteristic of the solvent and E is the energy gap between the emitting electronic state and the highest lying component of the next lower lying f state. Riseberg and Moos [14] found that this equation fit the non-radiative decay rates of lanthanide ions in crystalline hosts. Carnall has reviewed the applicability of this multiphonon relaxation model to aquo lanthanide ion fluorescence and noted that the order of the multiphonon process needed to be less than 5 or 6 to compete effectively with radiative decay [15]. The order of the process is given by the ratio E/a. In solutions the assumption is that non-radiative decay of the metal-centered electronic excitation occurs primarily via coupling to vibrational modes of inner coordination sphere ligands which are water molecules in the case of aquo metal cations. Stein and Wurzberg [13] have noted that the multiphonon decay mechanism (Eqn 2) predominates for lanthanide ion non-radiative decay processes with orders between roughly 3 and 6 (i.e. for the largest energy gap fluorescing transitions in Sm, Eu, Tb and Dy). For these reasons we have chosen to compare the Es

and Cm non-radiative decay rates with those for the similar energy gap lanthanide ions Sm, Eu, Tb and Dy.

If non-radiative decay occurs primarily via energy transfer to vibrational modes of inner coordination sphere water molecules, the observed non-radiative decay rates would be expected to be markedly reduced when deuterium is substituted for hydrogen in the solvent due to the reduced ligand vibrational mode energies. From Eqn 2, one expects $\log(k_{nr})$ for a given ion to decrease by a factor of about 1.35 on deuterating the solvent. This assumes that the parameter, a, in Eqn 2 is proportional to the inverse of the energy of a quantum of the stretching vibrational modes of water (circa 44.3 kJ/mole for H_2O and 32.6 kJ/mole for D_2O). The prediction then is that the ratio of the slopes of the dashed lines or of the solid lines in Figure 3 should be about 1/1.35 or 0.74, dividing the slope for the H_2O solution by the slope for the D_2O solution. The lanthanide data give a slope ratio of 0.75 whereas the actinide data give a ratio of 0.52. The small slope ratio for the actinides is clearly inconsistent with Eqn 2.

More detailed models of non-radiative decay rates such as that of Sturge [16] directly account for the coupling strength, S, of the metal ion excited state with its environment. For intermediate coupling strengths (S of order 1), Sturge's model predicts that a log (non-radiative decay rate) versus order parameter plot will be curved such that its slope increases with increasing value of the

order parameter. While the An^{3+} data in Figure 3 are too limited to allow detailed comparison with theoretical models such as that of Sturge, it is evident that trends predicted for intermediate coupling strength are found in the actinide data: decreasing effect of deuteration as energy gap decreases and larger non-radiative decay rates in comparison with the classic weak coupling case, lanthanide ion 4f state non-radiative decay. It is unfortunate that there are no An^{3+} ion 5f states with energy gaps between those of Es^{3+} and Cm^{3+}.

Opportunities for further exploration of An^{3+} 5f state non-radiative decay abound at smaller energy gaps. Study of such transitions will be challenging due to extremely small quantum yields and nanosecond or shorter time scale fluorescence lifetimes. Achieving a predictive understanding of actinide ion non-radiative decay is fundamental to assessing the utilization of fluorescence detection in monitoring transuranic ions in solution at environmentally relevant concentrations and will require systematic consideration of the interaction of 5f electron states with inner coordination sphere ligands. The present study of aquo and complexed Es^{3+} fluorescence marks the beginning of such systematic studies.

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TABLE I. Observed Fluorescence Lifetimes of the First Excited J = 5 State State of Es^{3+} in Selected Solution Environments.

Solvent	Acid	Acid Concentration (mol/dm^3)	Es^{3+} Concentration (mol/dm^3)	Fluorescence Lifetime (microseconds)[a]
D_2O	DCl	0.5	1×10^{-3}	2.35 ± 0.02
			2×10^{-4}	2.70 ± 0.04
			3×10^{-5}	2.78 ± 0.03
			5×10^{-6}	2.87 ± 0.09
H_2O	HCl	0.5	2×10^{-4}	1.05 ± 0.05
n-heptane[b]			2×10^{-4}	2.34 ± 0.04

[a] Uncertainties shown are 1 standard deviation based on replicate determination of the lifetime for a given solution.

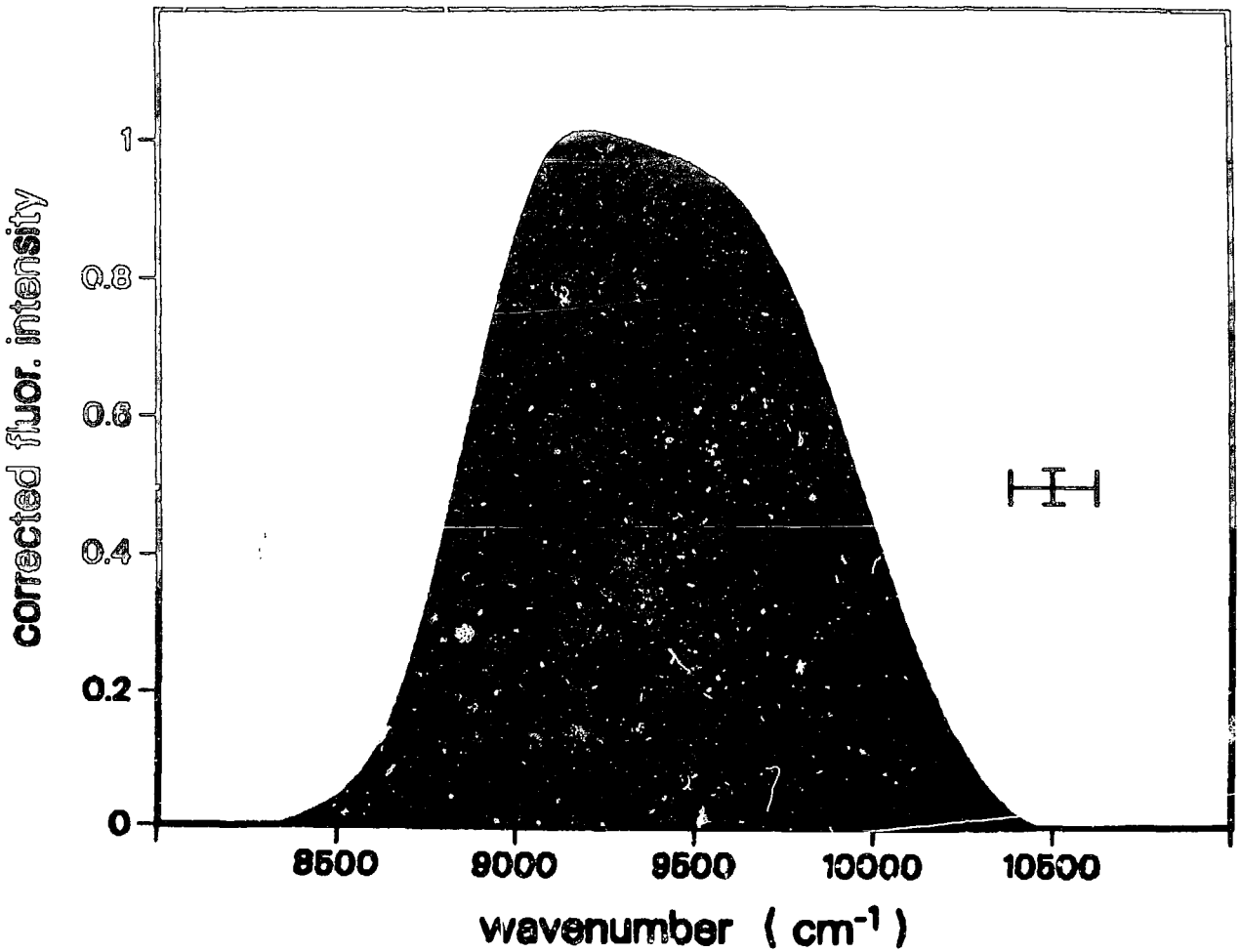
[b] See text. Es^{3+} was complexed with 1 formal HDEHP.

FIGURE CAPTIONS

1. Fluorescence emission spectrum of 1 x 10^{-3} mol/dm^3 $^{253}Es^{3+}$ in 0.6 mol/dm^3 DCl solution, 495 nm excitation, corrected for the spectral response of the fluorescence detection system. The spectral bandpass (full width half maximum) and fluorescence intensity uncertainty are shown.

2. Comparison of 5f state energies of Es^{3+} to the fluorescence excitation and emission energies. The J values of the 5f states are shown. The bold vertical arrow corresponds to the pump laser photon energy and the downward pointing arrow to the photon energy of the fluorescence emission. Some of the non-radiative processes are shown as wavy arrows.

3. The non-radiative decay rates, k_{nr}, of selected aquo lanthanide and actinide ions are plotted as function of the energy gap of the emitting f state in H_2O and D_2O solutions. The dashed and solid lines are linear least squares fits of the non-radiative decay data for lanthanides and actinides, respectively, to the simple energy gap law expression shown in Eqn 2.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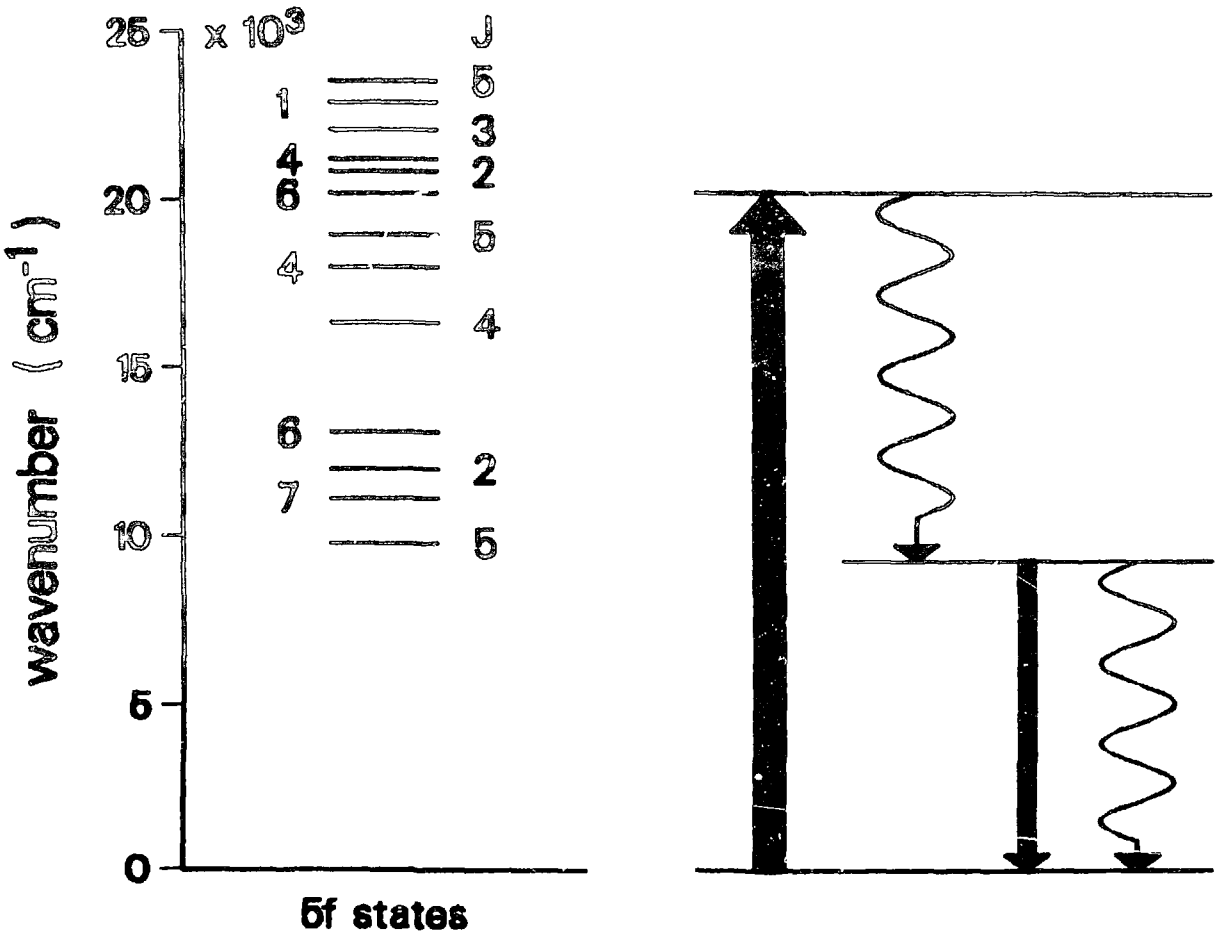
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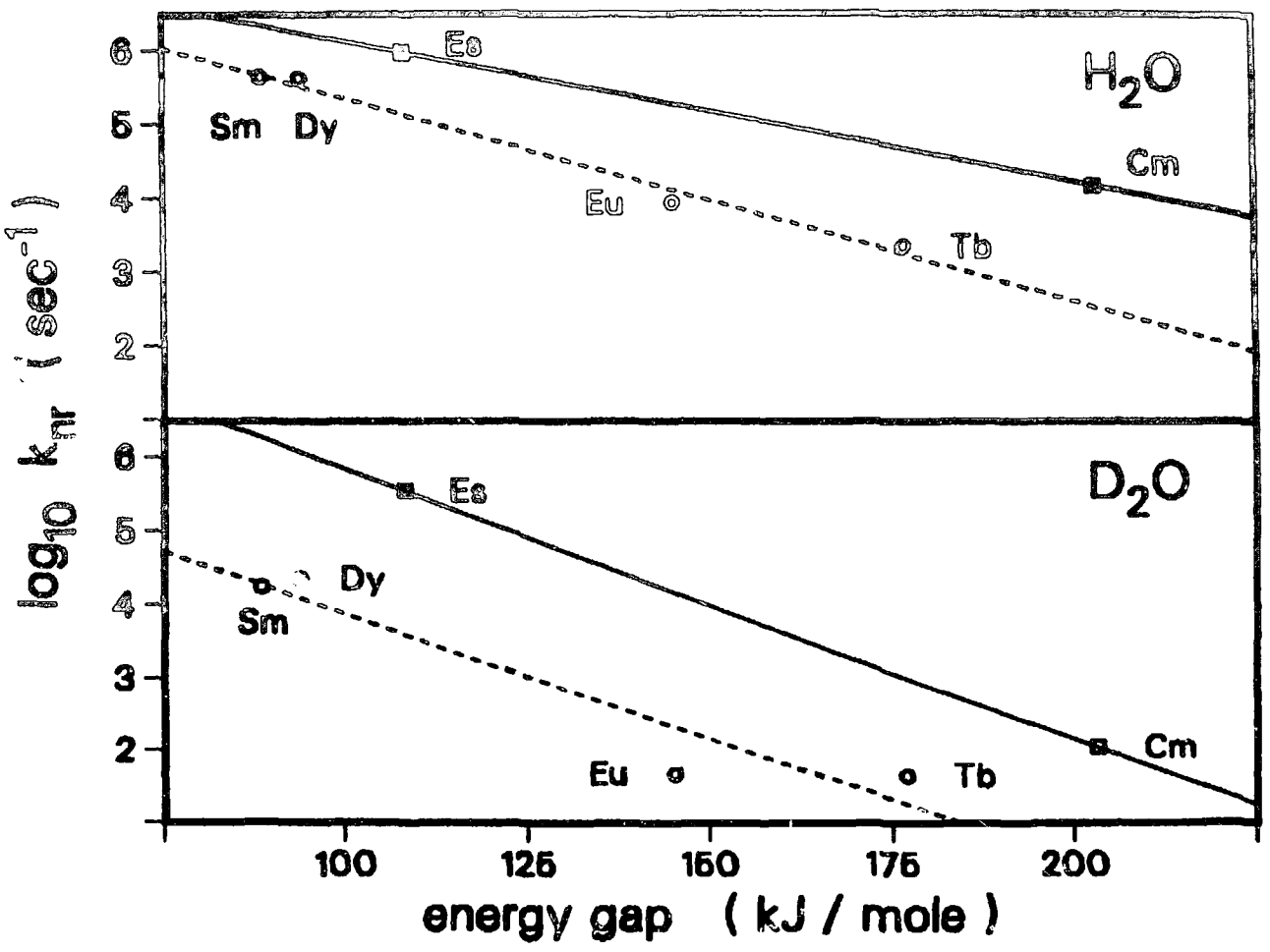
H_2O
D_2O
Es
Cm
Sm
Dy
Eu
Tb
$\log_{10} k_{nr}$ (sec^{-1})
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4
3
2
100
125
150
175
200
energy gap (kJ / mole)